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(54) Title: A LOW OUTGASSING AND NON-CROSSLINKING SERIES OF POLYMERS FOR EUV NEGATIVE TONE PHOTORESISTS

(57) Abstract: A series structure of a chemically amplified negative tone photoresist that is not based on cross-linking chemistry is herein described. The photoresist may comprise: a first aromatic structure copolymerized with a cycloolefin, wherein the cycloolefin is functionalized with a di-ol. The photoresist may also include a photo acid generator (PAG). When at least a portion of the negative tone photoresist is exposed to light (EUV or UV radiation), the PAG releases an acid, which reacts with the functionalized diol to rearrange into a ketone or aldehyde. Then new ketone or aldehyde is less soluble in developer solution, resulting in a negative tone photoresist.

**A LOW OUTGASSING AND NON-CROSSLINKING SERIES OF POLYMERS FOR
EUV NEGATIVE TONE PHOTORESISTS**

FIELD

[0001] This invention relates to the field of fabricating semiconductor devices and, in particular, to negative tone photoresists.

BACKGROUND

[0002] Modern integrated circuits generally contain several layers of interconnect structures fabricated above a substrate. The substrate may have active devices and/or conductors that are connected by the interconnect structure. As these devices become smaller the need for fine patterning through photolithography has become increasingly more important.

[0003] To obtain the fine patterns needed for the current generation of devices, KrF (248nm) and ArF (193nm) lasers are being used. The dimension of device will continue to scale down, and may require even shorter wavelengths, such as EUV (13.4nm). To obtain smaller and finer patterns through the use of shorter wavelength light sources, a new generation of photoresists will be required. The design of the next generation of photoresist may be governed by limitation with EUV tools, such as flare.

[0004] When extreme ultraviolet (EUV) steppers are used to expose photoresist to radiation with a wavelength of 13.4nm, the mid frequency roughness of the optics will cause flare. Flare is produced when the light

source is reflected off the reflective optics and passes through the mask to expose the photoresist material, and will reduce the contrast of the aerial image. Small amounts of flare may be able to be corrected for by calculating the amount of flare that will occur and scaling the mask CDs accordingly; however, for higher amounts of flare, alternative strategies are necessary. One strategy is the use of a negative tone resist, especially for poly layers, because the amount of flare is proportional to the amount of light that passes through the mask.

[0005] A positive tone photoresist becomes more soluble to a developer solution upon exposure to light, whereas a negative tone photoresist becomes less soluble to a developer solution upon exposure to light. Consequently, when a negative photoresist is used at the poly layer, a dark field mask, instead of a bright field mask, may be used to create a dark field pattern. By using a dark field mask the impact of flare on an underlying layer may be significantly reduced.

[0006] Current negative tone photoresists utilize a cross-linking mechanism that makes the exposed portion of the photoresist less soluble to the base developer solution. As cross-linking occurs, the molecular weight of the polymer will decrease. However swelling may occur, since the change in solubility is governed by a change in the molecular weight, and the interactions between the resist and the developer are still very favorable.

Swelling of the resist structures will prevent correct pattern transfer and affect the resolution.

[0007] Because of these limitations, there is a need for a negative tone photoresist that does not swell during the developing process, thereby, allowing the use of a dark field mask to reduce the effect of flare in patterning.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The present invention is illustrated by way of example and not intended to be limited by the figures of the accompanying drawings.

[0009] Figure 1 illustrates a copolymer structure that may be used as a negative tone resist.

[0010] Figure 2 is a cross-sectional elevation view of a photoresist layer that has been deposited on an underlying layer.

[0011] Figure 3 is a cross-sectional elevation view of Figure 2 after at least a portion of the photoresist layer has been exposed to radiation through a mask.

[0012] Figure 4 is the chemical rearrangement that occurs in the exposed portions of the photoresist layer in Figure 3.

[0013] Figure 5 is a cross-sectional elevation view of Figure 3 after the photoresist layer has been developed in a developer solution.

[0014] Figure 6 is a cross-sectional elevation view of Figure 5 after trenches have been etched in the underlying layer from Figure 6.

[0015] Figure 7 is a cross-sectional elevation view of Figure 6 after the remaining photoresist layer has been stripped.

DETAILED DESCRIPTION

[0016] In the following description, numerous specific details are set forth such as examples of specific developer solutions in order to provide a thorough understanding of the present invention. It will be apparent, however, to one skilled in the art that these specific details need not be employed to practice the present invention. In other instances, well known methods and materials, such as polymerization techniques for fabricating the polymer, spin-coating techniques, chemical amplification strategies, and stripping techniques have not been described in detail in order to avoid unnecessarily obscuring the present invention.

[0017] Figure 1 illustrates the chemical structure of copolymer 100 that may be used as the basis of a negative tone photoresist. Copolymer 100 includes first aromatic monomer 105 copolymerized with cycloolefin monomer 110. First aromatic structure 105 may be any aromatic structure, such as benzene and may have a functional group R1 bonded in any position to aromatic structure 105. R1 may be altered to change resist properties,

such as the adhesion and/or dissolution characteristics of the photoresist. R1 may be a hydrogen atom, an alkyl group, or a hydroxyl group.

[0018] Cycloolefin 110 may be any cycloolefin, such as a second aromatic structure or a norbonene structure. The chemical structure of cycloolefin 110 may be varied by changing the functional group X. As an example, X may be no atom (i.e. an aromatic structure), a carbon atom (norbornene), an alkyl, an oxygen atom, or a sulfur atom.

[0019] Cycloolefin 110 may be functionalized with di-ol 115. Di-ol 115 may be an alkyl group with two hydroxyls groups that are bonded to cycloolefin 110.

[0020] In addition, di-ol 115 may have additional functional groups, R2, R3, and R4 bonded to it. The selection of functional groups R2, R3, and R4, will affect the resist properties, such as dissolution, adhesion, and etch resistance. For example, R2, R3, and R4 may be individually selected from any of the following: hydrogen, alkyl, aromatic, or cage groups. As another illustrative example, if a cage is used for either one or all of R2, R3, and R4, the etch resistance of the photoresist material may be increased.

[0021] It is readily apparent that the photoresist may include other elements and structures. For example the negative tone photoresist may include a photoacid generator (PAG) to facilitate chemical amplification. Chemical amplification is discussed in more detail in reference to Figures 5

and 6. As illustrative example, the PAG may be an iodonium, sulfonium, or a non-ionic PAG. The PAG may be used to release the necessary acid, such as an H⁺ acid, when exposed to light.

[0022] Turning to **Figures 2-7**, an illustrative method of how a photoresist comprising copolymer 100 may be used is depicted. As illustrated in **Figure 2**, a photoresist layer 210 is deposited on an underlying layer, such as underlying layer 215, in step 205. Photoresist layer 210 may contain copolymer 100, illustrated in **Figure 1**, casting solvents, such as propylene glycol methyl ether acetate (PGMEA), and/or ethyl lactate (EL), and the other necessary components such as PAGs, base quenchers and/or surfactants. Photoresist layer 210 may be deposited by a spin-coating technique onto underlying layer 215. Underlying layer 215 may be any substrate that is used at different layers in the manufacturing of devices, such as silicon, or polysilicon, and it may contain other structures such as gates, local interconnects, metal layers, or other active/passive device structures or layers.

[0023] In reference to **Figure 3**, in step 305, exposed portions 515 and 520 of photoresist layer 210 are exposed to radiation, which may be EUV radiation (13.4nm), but may also be any other wavelength radiation, such as 248nm or 193nm. As described later, step 305 may also include baking and other processes to facilitate chemical amplification. Radiation exposure may

occur through mask 310 so that only some sections of the photoresist are exposed, such as exposed portions 315 and 320. Exposed portions 315 and 320 may undergo a pinacol rearrangement, as described in reference to

Figure 6.

[0024] As mentioned above, exposure chemistry in step 305 may occur via a chemical amplification strategy. To increase the sensitivity of the photoresist (i.e. reduce the amount of radiation needed to cause the necessary chemical reaction in the exposed portions 315 and 320) the photoresist may be chemically amplified. Chemical amplification occurs when a PAG reacts during exposure to produce an acid catalyst. The acid catalyst then mediates a cascade of reactions as it diffuses through the resist. A post exposure bake (PEB) step may occur after the exposure step to increase the diffusion length of the acid catalyst.

[0025] **Figure 4** illustrates the chemistry that will occur in the presence of the acid catalyst to change the solubility of the copolymer. A pinacol rearrangement may occur due to the presence of an acid in exposed portions 315 and 320, shown in **Figure 3**. The general pinacol rearrangement chemistry is well known and discussed in, "H. Bosshard, M.E. Baumann and G. Schetty, *Helv. Chim. Acta.*, 53, 1271 (1970)," and "T.E. Zalesskaya and I.K. Lavorva, *JOC, USSR*, 4, 1999 (1968)." Diol 115 reacts with an H⁺ acid to form a carbonate containing material, such as a ketone or an aldehyde 410 and a

water by-product 415. They H+ acid 405 may be regenerated after the pinacol rearrangement, and may continue to diffuse through the resist to mediate further reactions. After rearrangement, functional groups R2, R3, and R4 will be bonded to the resulting ketone or aldehyde 410. The R3 functional group will be bonded to a different carbon after the reaction, consistent with the chemistry of pinacol rearrangement.

[0026] Step 305 may also include the generation of water 415. If the pinacol arrangement deprotection occurs while the resist is still under vacuum in the EUV tool, the water may outgas. Outgassing is in general considered very problematic, because it can contaminate the optics. However early research shows that the presence of water or oxygen in the chamber may actually help to clean EUV optics. However high concentrations of water can cause oxidation of the optics, which will damage the optics. The optics may be protected from oxidation by the use of capping layers that are known in the art.

[0027] [0028] Another method for protecting the optics from oxidation is to design copolymer 100 so that the pinacol rearrangement deprotection has a high activation energy. For reactions with high activation energies, the pinacol rearrangement deprotection will only occur at high temperatures. In this case the acid will be generated under exposure, but the deprotection will not occur until after the wafer has been removed from the

exposure toll and is subjected to a PEB. Water that is generated during the PEB may outgas during the PEB, but this should not be problematic since water will not cause damage to the bake tools. The polymer can be designed to have a high deprotection energy for the pinacol rearrangement by selecting the correct functional groups R₂, R₃, and R₄, such as alkyl groups.

[0028] As shown in **Figure 5**, the newly generated ketone or aldehyde 410, shown in **Figure 4**, may be less soluble in an aqueous base developer solution. In step 505, the less soluble exposed portions 315 and 320, when developed in developer solution will remain, while the rest of the photoresist layer 210, depicted in **Figure 3**, will be removed by the developer solution. As an illustrative example, 2.38% tetra-methyl ammonium hydroxide (TMAH) may be used as the developer solution. Therefore, a pattern on a mask, such as mask 310 in **Figure 3**, may be transferred onto underlying layer 305 with the use of the aforementioned negative tone photoresist.

[0029] **Figure 6 and 7** illustrate a single example of how this negative tone photoresist may be used. However, it is readily apparent that many other processing steps may be used to transfer the pattern from the photoresist to the substrate, such as ion implantation instead of/in addition to the steps depicted in **Figure 6** and **Figure 7**. Turning to **Figure 6**, in step 605, common etchants may be used to etch via openings and/or trenches,

such as trenches 610, while exposed portions 315 and 320 remain. Exposed portions 315 and 320 may protect the portions of underlying layer 215 that are beneath exposed portions 315 and 320.

[0030] In reference to **Figure 7**, exposed portions 315 and 320, shown in **Figure 6**, may be stripped away leaving underlying layer 215, with trenches 610. Common photoresist stripping methods may be used to remove exposed portions 315 and 320.

[0031] Therefore, as shown above, a negative tone photoresist that is not based on cross-linking chemistry may be made and used. Negative photoresist may have applications at EUV wavelengths to reduce flare. Negative tone resists will reduce flare, because a dark field mask can be used at the poly layer, which reduces flare compared to a bright field mask. The deprotection chemistry may show improved performance over current negative resists based on cross-linking chemistry because swelling may be lower. When portions of the photoresist are exposed to light, the PAGs may generate acids. These acids may react with the di-ol deprotecting group to form ketone/aldehyde and water. The newly generated ketone or aldehyde is less soluble in a developer solution, such as 2.38% TMAH, than the original diol. Consequently, the photoresist that was not exposed will dissolve in the developer solution, while the exposed portions will not dissolve leaving the exposed portions of the photoresist.

[0032] In the foregoing specification, the invention has been described with reference to specific exemplary embodiments thereof. It will, however, be evident that various modifications and changes may be made thereto without departing from the broader spirit and scope of the invention as set forth in the appended claims. The specification and drawings are, accordingly, to be regarded in an illustrative sense rather than a restrictive sense.

CLAIMS

What is claimed is:

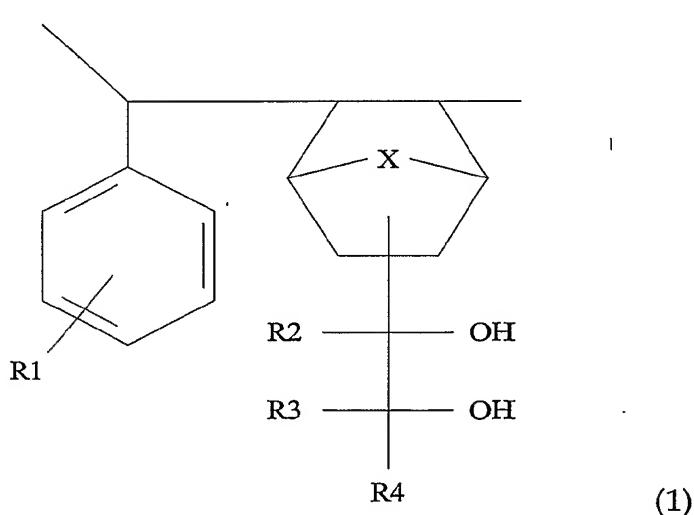
1. A photoresist comprising:
a cycloolefin functionalized with a di-ol.
2. The photoresist of claim 1, further comprising:
an aromatic structure copolymerized with the cycloolefin.
3. The photoresist of claim 2, further comprising a molecule bonded to
the aromatic structure, wherein the molecule is selected from a group
consisting of a hydrogen atom, an alkyl group, or a hydroxyl group.
4. The photoresist of claim 1, wherein the di-ol comprises an alkyl
functionalized by two hydroxyl groups.
5. The photoresist of claim 1, wherein the di-ol further comprises
additional functional groups, each functional group being selected
from a group consisting of a hydrogen atom, an alkyl group, an
aromatic structure, or a cage.
6. The photoresist of claim 1, wherein the cycloolefin is an aromatic
structure.

7. The photoresist of claim 1, wherein the cycloolefin is a norbornene structure.

8. The photoresist of claim 7, wherein the norbornene structure comprises a side-group, wherein the side-group is selected from a group consisting of a carbon atom, and alkyl group, an oxygen atom, or a sulfur atom.

9. The photoresist of claim 2, further comprising a photo acid generator (PAG).

10. A photoresist comprising:
a copolymerized structure represented by the following molecule



where R1 is a hydrogen atom, an alkyl, or a hydroxyl, where each of R2, R3 and R4 is a hydrogen atom, alkyl, aromatic, and/or cage, and

where X is no atom, a carbon atom, an alkyl, an oxygen atom, or a sulfur atom.

11. A method comprising:

depositing a photoresist comprising a cycloolefin functionalized with a di-ol on an underlying layer; and
exposing at least a portion of the photoresist to radiation to form at least a carbonate containing material.

12. The method of claim 11, wherein the carbonate containing material is a ketone.

13. The method of claim 11, wherein the carbonate containing material is a aldehyde.

14. The method of claim 11, wherein the underlying layer is a substrate.

15. The method of claim 11, wherein the photoresist is a negative tone photoresist.

16. The method of claim 11, wherein exposing at least a portion of the photoresist to radiation is done through a mask.

17. The method of claim 11, wherein the radiation is generated from an EUV exposure tool.

18. The method of claim 11, further comprising baking the photoresist.

19. The method of claim 11, wherein the photoresist further comprises a first aromatic structure copolymerized with the cycloolefin.

20. The method of claim 19, wherein the first aromatic structure is functionalized with a first functional group.

21. The method of claim 20, wherein the first functional group is selected from a group consisting of a hydrogen atom, an alkyl group, or a hydroxyl group.

22. The method of claim 19, wherein the di-ol comprises an alkyl functionalized by two hydroxyl groups.

23. The method of claim 22, wherein the di-ol further comprises a second, a third, and a fourth functional group, wherein each of the second, third, and fourth functional groups is a hydrogen atom, an alkyl group, an aromatic structure, or a cage.

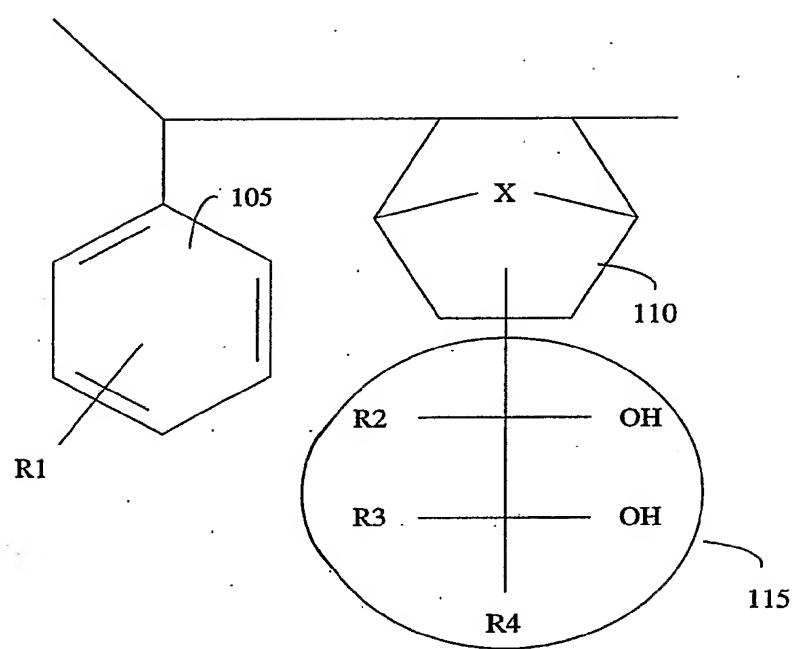
24. The method of claim 11, wherein depositing the photoresist on an underlying layer comprises: spin-coating the photoresist on the underlying layer.

25. The method of claim 11, further comprising developing the photoresist layer by depositing a developer solution on the photoresist layer.

26. The method of claim 25, wherein the developer is TMAH.

27. The method of claim 26, wherein the developer is 2.38% TMAH.

28. The method of claim 25, further comprising stripping the at least a portion of the photoresist layer exposed to UV rays.

1/5**FIG. 1**

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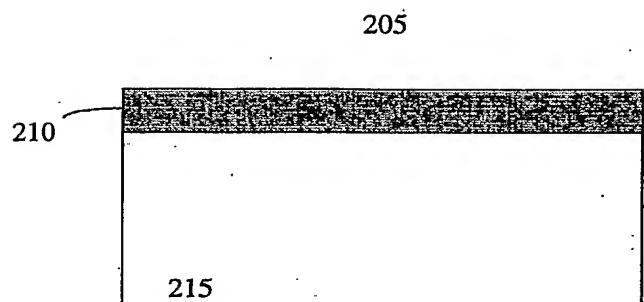


FIG. 2

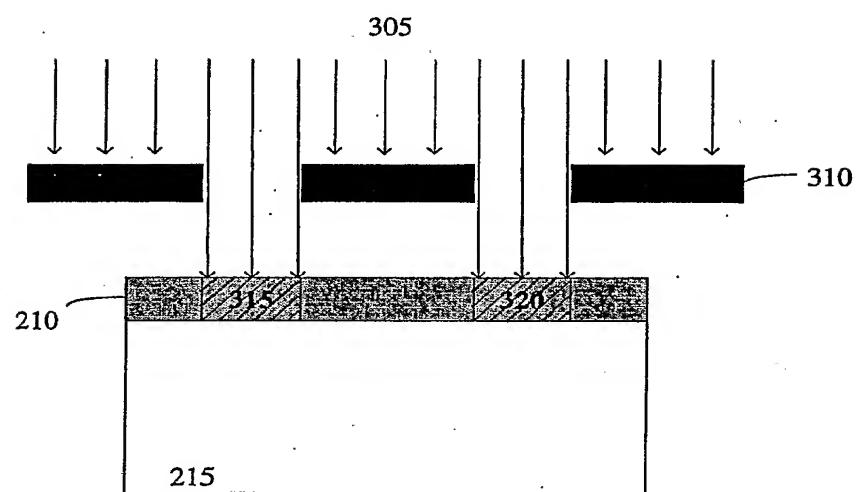


FIG. 3

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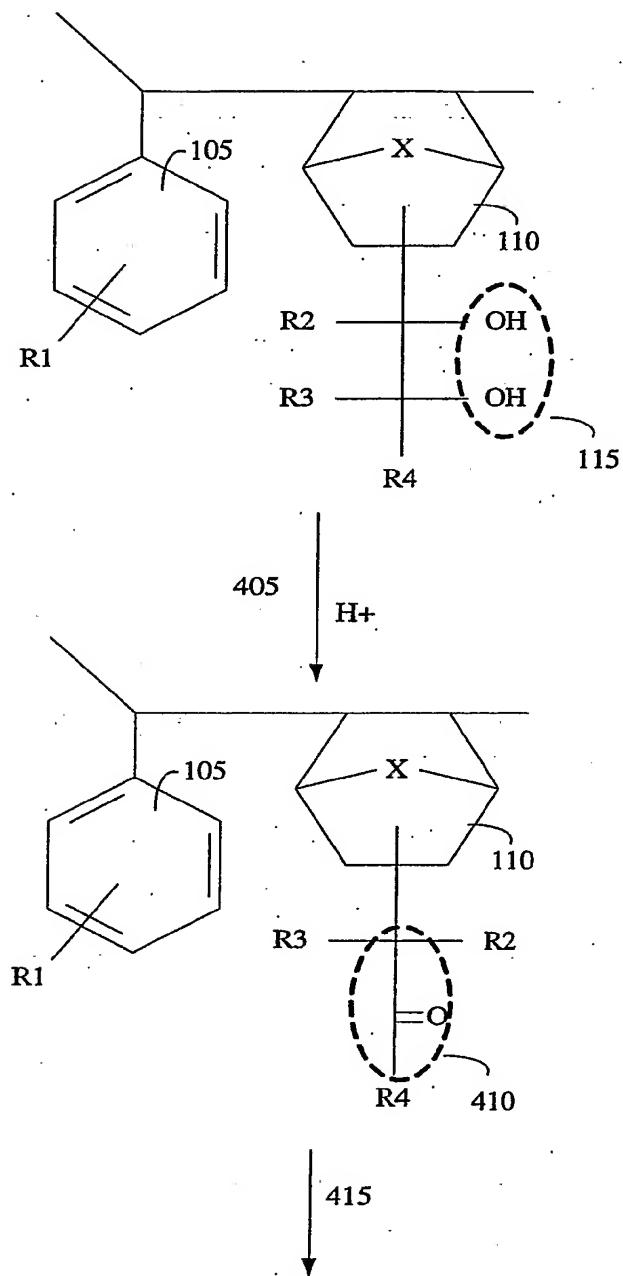


FIG. 4

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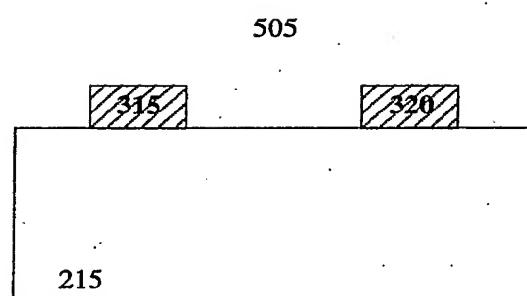


FIG. 5

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605

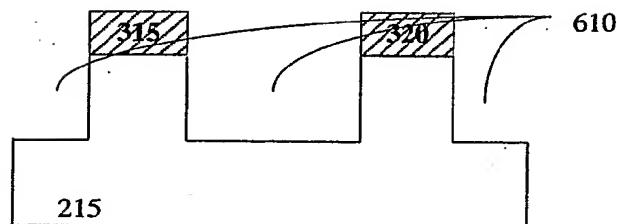


FIG. 6

705

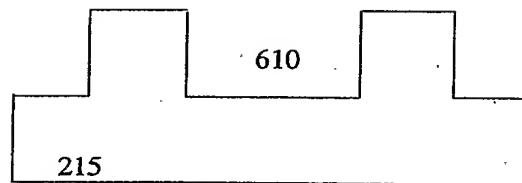


FIG. 7